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**APPLICATION NUMBER: 60/525,578**  
**FILING DATE: November 26, 2003**  
**RELATED PCT APPLICATION NUMBER: PCT/US04/39515**

Certified by



Jon W Dudas

Acting Under Secretary of Commerce  
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**PROVISIONAL APPLICATION FOR PATENT COVER SHEET**

This is a request for filing a PROVISIONAL APPLICATION FOR PATENT under 37 CFR 1.53(c).

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60/525578



INVENTOR(S)					
Given Name (first and middle [if any])		Family Name or Surname		Residence (City and either State or Foreign Country)	
Keith R.		Minnich		Pewaukee, Wisconsin	
Additional inventors are being named on the <u>2 of 2</u> separately numbered sheets attached hereto					
TITLE OF THE INVENTION (500 characters max)					
Direct all correspondence to: <b>CORRESPONDENCE ADDRESS</b>					
<input checked="" type="checkbox"/> Customer Number: <u>26753</u>					
OR					
<input type="checkbox"/> Firm or Individual Name		Thomas M. Wozny			
Address		Andrus, Sceales, Starke & Sawall, LLP			
Address		100 East Wisconsin Avenue, Suite 1100			
City		Milwaukee	State	WI	Zip 53202-4178
Country		USA	Telephone	414-271-7590	Fax 414-271-5770
<b>ENCLOSED APPLICATION PARTS (check all that apply)</b>					
<input checked="" type="checkbox"/> Specification Number of Pages <u>6</u>		<input type="checkbox"/> CD(s), Number _____			
<input checked="" type="checkbox"/> Drawing(s) Number of Sheets <u>1</u>		<input checked="" type="checkbox"/> Other (specify) <u>Return Receipt Postcard</u>			
<input type="checkbox"/> Application Date Sheet. See 37 CFR 1.76					
METHOD OF PAYMENT OF FILING FEES FOR THIS PROVISIONAL APPLICATION FOR PATENT					
<input checked="" type="checkbox"/> Applicant claims small entity status. See 37 CFR 1.27.		<b>FILING FEE Amount (\$)</b>  <u>\$80.00</u>			
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[Page 1 of 2]

Respectfully submitted,

SIGNATURE

TYPED or PRINTED NAME Thomas M. Wozny

TELEPHONE 414-271-7590

Date November 26, 2003

REGISTRATION NO. 28,922

(if appropriate)

Docket Number: 4553-00005

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PTO/SB/16 (08-03)

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**[Page 2 of 2]**

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# FEE TRANSMITTAL for FY 2004

Effective 10/01/2003. Patent fees are subject to annual revision.

☒ Applicant claims small entity status. See 37 CFR 1.27

TOTAL AMOUNT OF PAYMENT (\$ 80.00

## Complete if Known

Application Number  
Filing Date  
First Named Inventor Keith R. Minnich  
Examiner Name  
Art Unit  
Attorney Docket No. 4553-00005

## METHOD OF PAYMENT (check all that apply)

☒ Check ☐ Credit card ☐ Money Order ☐ Other ☐ None

☐ Deposit Account:

Deposit Account Number 01.2000  
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## FEE CALCULATION

### 1. BASIC FILING FEE

Large Entity Fee Code (\$)	Small Entity Fee Code (\$)	Fee Description	Fee Paid
1001 770	2001 385	Utility filing fee	
1002 340	2002 170	Design filing fee	
1003 530	2003 265	Plant filing fee	
1004 770	2004 385	Reissue filing fee	
1005 160	2005 80	Provisional filing fee	\$80.00
SUBTOTAL (1)			(\$ 80.00

### 2. EXTRA CLAIM FEES FOR UTILITY AND REISSUE

Total Claims  -20\*\* =  X  =  0  
Independent Claims  -3\*\* =  X  =  0  
Multiple Dependent  =  0

Large Entity Fee Code (\$)	Small Entity Fee Code (\$)	Fee Description
1202 18	2202 9	Claims in excess of 20
1201 86	2201 43	Independent claims in excess of 3
1203 290	2203 145	Multiple dependent claim, if not paid
1204 86	2204 43	** Reissue independent claims over original patent
1205 18	2205 9	** Reissue claims in excess of 20 and over original patent

SUBTOTAL (2) (\$ 0.00

\*\*or number previously paid, if greater; For Reissues, see above

## FEE CALCULATION (continued)

### 3. ADDITIONAL FEES

Large Entity Small Entity

Fee Code (\$)	Fee Code (\$)	Fee Description	Fee Paid
1051 130	2051 65	Surcharge - late filing fee or oath	
1052 50	2052 25	Surcharge - late provisional filing fee or cover sheet	
1053 130	1053 130	Non-English specification	
1812 2,520	1812 2,520	For filing a request for ex parte reexamination	
1804 920*	1804 920*	Requesting publication of SIR prior to Examiner action	
1805 1,840*	1805 1,840*	Requesting publication of SIR after Examiner action	
1251 110	2251 55	Extension for reply within first month	
1252 420	2252 210	Extension for reply within second month	
1253 950	2253 475	Extension for reply within third month	
1254 1,480	2254 740	Extension for reply within fourth month	
1255 2,010	2255 1,005	Extension for reply within fifth month	
1401 330	2401 165	Notice of Appeal	
1402 330	2402 165	Filing a brief in support of an appeal	
1403 290	2403 145	Request for oral hearing	
1451 1,510	1451 1,510	Petition to institute a public use proceeding	
1452 110	2452 55	Petition to revive - unavoidable	
1453 1,330	2453 665	Petition to revive - unintentional	
1501 1,330	2501 665	Utility issue fee (or reissue)	
1502 480	2502 240	Design issue fee	
1503 640	2503 320	Plant issue fee	
1460 130	1460 130	Petitions to the Commissioner	
1807 50	1807 50	Processing fee under 37 CFR 1.17(q)	
1806 180	1806 180	Submission of Information Disclosure Stmt	
8021 40	8021 40	Recording each patent assignment per property (times number of properties)	
1809 770	2809 385	Filing a submission after final rejection (37 CFR 1.129(a))	
1810 770	2810 385	For each additional invention to be examined (37 CFR 1.129(b))	
1801 770	2801 385	Request for Continued Examination (RCE)	
1802 900	1802 900	Request for expedited examination of a design application	

Other fee (specify)

\*Reduced by Basic Filing Fee Paid

SUBTOTAL (3) (\$ 0.00

## SUBMITTED BY

Name (Print/Type) Thomas M. Wozny Registration No. 28,922 Telephone  
Signature *Thomas M. Wozny* (Attorney/Agent) Date November 26, 2003

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METHOD FOR PRODUCTION OF HIGH PRESSURE STEAM FROM  
PRODUCED WATER WITH ZERO LIQUID DISCHARGE

Inventors: Keith R. Minnich  
Mark C. Nicholson  
RamKumar Karlapudi  
Richard M. Schoen

*Attorneys for Applicant:*  
*Andrus, Sceales, Starke & Sawall, LLP*  
*100 East Wisconsin Avenue, Suite 1100*  
*Milwaukee, Wisconsin 53202-4178*  
*(414) 271-7590*  
*Fax: (414) 271-5770*  
*Attorney Docket No.: 4553-00005*

# METHOD FOR PRODUCTION OF HIGH PRESSURE STEAM FROM PRODUCED WATER WITH ZERO LIQUID DISCHARGE

## BACKGROUND OF THE INVENTION

**[0001]** The present invention relates to using produced water obtained from oil well production fluids to generate steam, and more particularly to an evaporation based zero liquid discharge (ZLD) method for generation of high pressure steam from produced water.

**[0002]** The injection of steam into geologic formations to permit or enhance the recovery of fossil fuels is an established practice. The steam is typically generated in special purpose steam generators from produced water. The current practice has several disadvantages:

**[0003]** 1. The produced water requires treatment that generates large quantities of waste for disposal.

**[0004]** 2. Only a portion of the produced water can be recovered. A source of clean makeup water is required to replace the produced water that cannot be recovered.

**[0005]** 3. The produced water that is not recovered becomes a waste that must be disposed.

**[0006]** 4. Even after treatment, the produced water can cause scaling or fouling in the steam generator which degrades the steam generation performance and requires significant maintenance and cleaning.

## SUMMARY OF THE INVENTION

**[0007]** An evaporation based ZLD method for generation of 100% high pressure steam from produced water in the heavy oil production industry. De-oiled produced water is processed through an ion exchange system to remove multivalent cations, acidified if necessary, and then decarbonated prior to treatment in a high pH/high pressure evaporator. The vapor produced is suitable, as is, for the steam assisted gravity drainage (SAGD) method which is being utilized by heavy oil

recovery installations. Evaporator blowdown is further treated in a crystallizer to provide a ZLD system. Recovery ratios in excess of 98% are achievable with most produced waters.

[0008] The process described herein has the following advantages over current practice:

[0009] 1. A conventional boiler can be used to convert fossil fuel to steam. The fired boiler operates on high quality demineralized water instead of produced water.

[0010] 2. Higher conversion of produced water to steam is possible.

[0011] 3. Essentially all of the produced water is converted to steam for injection.

[0012] 4. There is a very low wastewater production.

[0013] 5. The process can be complete Zero Liquid Discharge (ZLD).

[0014] 6. The amount of waste produced is less than what is produced by conventional lime soda softening processes.

[0015] 7. Much less energy is required for the process as compared to conventional evaporation technology.

[0016] 8. The process is suitable for high concentrations of silica in the produced water.

[0017] 9. The pH of the feed to the evaporation step is increased to a level where the heat transfer surface operates in a continuous cleaning mode and is not subject to fouling.

#### BRIEF DESCRIPTION OF THE DRAWINGS

[0018] In the drawings:

[0019] Fig. 1 is a flow diagram illustrating the zero liquid discharge process for production of high pressure steam from produced water in accordance with the present invention.



## DETAILED DESCRIPTION OF THE INVENTION

**[0020]** Produced water, which has been de-oiled according to standard practices, is stream 1. As is well known, "produced water" is water that has been extracted from oil well production fluid. Oil well production fluid refers to the fluid composition obtained from oil wells, and normally includes oil, natural gas and water as well as dissolved materials such as ionic salts, and gases, along with suspended solids, and bacteria. This fluid is treated to remove the gas and oil leaving a separated aqueous stream referred to as "produced water" which contains the above referred to dissolved/suspended materials. Produced water typically contains a ratio of about 2.5 parts water and 1 part oil.

**[0021]** Softener 2 removes the multivalent ions from the wastewater. The salts of these ions are only slightly soluble. These ions are removed to prevent scale formation in the evaporation steps. Softener 2 can be any of sodium zeolite, sodium form weak acid cation, or any combination of single or two stage sodium zeolite, or sodium form weak acid cation. Calcium, magnesium, strontium, barium, aluminum, iron, manganese and other multivalent ions are reduced to a low concentration. The softener is regenerated using concentrator distillate, stream 28, and regeneration chemicals stream 25. Softener 2 regeneration waste stream 27 is treated in crystallizer 19. The softened produced water is stream 3.

**[0022]** Stream 3 enters condenser 32. The vapor, stream 4, produced by evaporation in crystallizer 19, which is approximately 10% of the produced water flow, flows into condenser 32. Stream 4 condenses into stream 3 and creates stream 33. This allows recovery of essentially all the available produced water.

**[0023]** Acid (stream 31) is added to stream 33 to convert alkalinity to carbon dioxide. Stream 33 enters deaerator 5 where the non-hydroxide alkalinity, in the form of carbon dioxide, is reduced to a concentration that is below 10 ppm. The softened, carbonate alkalinity free, produced water is stream 6.

**[0024]** Caustic soda, stream 24, is added to stream 6 to raise the pH of the produced water.

- [0025] Stream 6 can be preheated by hot produced water, or other waste heat source, to improve the overall energy efficiency of the system.
- [0026] Stream 6 is mixed with boiler blowdown, stream 14, and then enters evaporator 10. At least 90% of stream 6 is evaporated to produce high pressure steam, stream 11, for injection. Stream 11 is essentially equal in flow to stream 1.
- [0027] Fuel, stream 7, is combusted in boiler 8 to produce steam, stream 9, which is condensed in evaporator 10. The condensed steam is returned as condensate, stream 12 to the boiler. A small portion of the condensate, less than 2%, is discharged as blowdown, stream 14. Demineralized water, stream 13, is added to boiler 8 to replace blowdown stream 14. Combustion gases, stream 29, can be further treated to remove pollutants.
- [0028] The 10% or less of stream 6 that is not converted into high pressure steam in evaporator 10 enters concentrator 16. Concentrator 16 can be one of or a combination of thin film, natural circulation, or forced circulation design. The heat transfer surface can either be a plate type or tube type. The concentrator is a multiple effect type evaporator. The tube orientation can be either vertical or horizontal. The concentrator is heated with steam flashed from stream 15 as the pressure of stream 15 is reduced upstream of concentrator 16.
- [0029] The vapor (steam) produced in concentrator 16 becomes stream 30 and is used to drive evaporation in crystallizer 19. The heating vapor, stream 30, condenses in the heating section of the crystallizer 19.
- [0030] The distillate, stream 17, from the concentrator 16 is flashed into the heating section of the crystallizer 19. The distillate, stream 17, and the condensed vapor (steam) of stream 30 are combined in crystallizer 19 and discharged into condenser 32.
- [0031] The concentrate from concentrator 16, stream 18, enters the crystallizer 19.
- [0032] Crystallizer 19 can be one of or a combination of natural circulation or forced circulation design. The heat transfer surface can either be a plate type or tube type. The tube orientation can be either vertical or horizontal. The

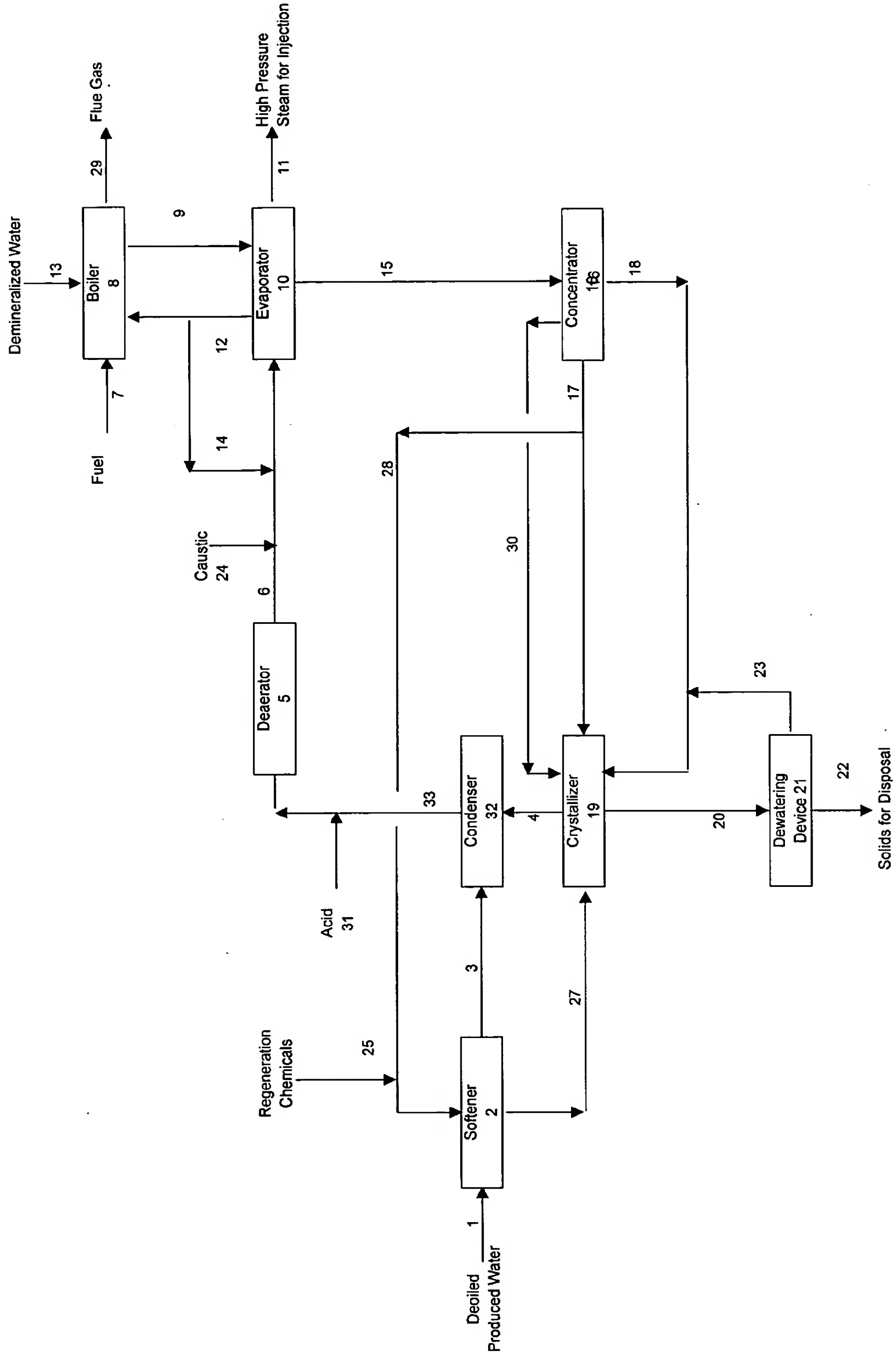
evaporator/crystallizer is direct heated with steam, stream 30, from concentrator 16. The concentrate, stream 20, which includes precipitated salts from the regenerant stream 27 and from evaporator discharge stream 18, from crystallizer 19 can be discharged to an onsite pond or dewatering device 21. Dewatering device 21 can be a belt press, filter press, centrifuge or other commercially available device. The discharge from dewatering device 21, stream 22, is suitable for handling as a solid material for offsite disposal. The filtrate from dewatering device 21, stream 23, is recycled to crystallizer 19.

## METHOD FOR PRODUCTION OF HIGH PRESSURE STEAM FROM PRODUCED WATER WITH ZERO LIQUID DISCHARGE

### ABSTRACT

An evaporation based zero liquid discharge method for generation of 100%  
5 quality high pressure steam from produced water in the heavy oil production  
industry. De-oiled produced water is processed through an ion exchange system to  
remove multivalent cations, acidified if necessary, and then decarbonated prior to  
treatment in a high pH/high pressure evaporator. The vapor produced is suitable, as  
is, for the steam assisted gravity drainage method being utilized by heavy oil  
10 recovery installations. Evaporator blowdown is further treated in a crystallizer to  
provide a zero liquid discharge system. Recovery ratios in excess of 98% are  
achievable with most produced waters.





Method for Production of Steam From Produce Water with Zero Liquid Discharge

Figure 1